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CONFIDENTIAL

**TITLE:** PRESSURE AND POWER DEPENDENCE IN THE INFRARED LASER PHOTOLYSIS OF  
1-CHLORO-1-FLUOROETHYLENE: EXPERIMENT AND MODELING CALCULATIONS

**MASTER**

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Pressure and power dependence in the infrared laser photolysis  
of 1-chloro-1-fluoroethylene: Experiment and modeling calculations

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Abstract

Dissociation of the title compound following infrared multiphoton excitation was monitored via infrared fluorescence of the products, either HCl\* or HF\*. Total dissociation yield and branching ratio were monitored as functions of, respectively, pressure and photolytic intensity. A rate equations model of the excitation and dissociation process is shown to be consistent with both sets of data.

Introduction

The pulsed infrared laser induced photochemistry of 1-chloro-1-fluoro ethylene was investigated as a system from which maximal information could be obtained. This molecule possesses two distinct absorption bands in the spectral region accessible with a CO<sub>2</sub> laser: the  $\nu_2$  CH<sub>2</sub> planar rock at  $\sim 10.63\mu$  and the first overtone of the  $\nu_1$ , out of plane CFCl wag.<sup>1</sup> Further, the molecule is capable of undergoing dissociation via two molecular channels



either of which may lead to vibrationally excited products.<sup>2</sup> By examining both the absolute yield and the branching ratio for reactions 1) as a function experimentally variable parameters, such as photon flux, wavelength and ambient pressure, a coherent picture of the mechanism of excitation and dissociation may be drawn.

Experimental

The photolytic source was a grating-tuned CO<sub>2</sub> TEA laser operated at 0.6 Hz, with a typical output of 0.85 J/pulse in a circular beam. Laser output consisted of a 45-nsec spike (FWHM) containing  $\sim 80\%$  of the pulse energy followed by a low intensity tail of  $\sim 0.5$   $\mu$ sec duration. Infrared pulses were directed into the center of the photolysis cell with an A.R. coated 200 nm Ge lens. The cell was a stainless steel flow cell fitted with NaCl entrance and exit windows, and a CaF<sub>2</sub> viewing window. Pressure was monitored with a Barocel capacitance manometer.

Infrared fluorescence was viewed at right angles to the laser beam by focusing it onto a cooled infrared detector. A variety of wide and narrow band interference filters, and gas filters could be inserted between the cell and detector. The signals were amplified, digitized (200 nsec pt<sup>-1</sup>) and averaged on a Z-80A based microcomputer.<sup>3</sup> Total response time of the system was found to be  $\sim 0.5$   $\mu$ sec. Typical experiments required from 50 to 2000 shots averaged, depending on pressure and fluence

Results and Discussion

Figure 2 shows infrared emission observed in the 2.0-2.7  $\mu$ m region (limits of the filter used). This signal rises instantaneously and exhibits a single exponential decay: it was assigned to HF emission. The signal shown in Figure 3 was acquired in the 3.1-4.1  $\mu$ m region and consists of an instantaneous rise and double exponential decay. The fast falling signal is likely due to quasicontinuum emission, while the slow signal was found to be due to HCl fluorescence. Extrapolation to  $t=0$  of the semilog fluorescence signals from HF and HCl was used to monitor the yield of each product.

Figure 4 shows the dependence of the HF signal on the pressure of added N<sub>2</sub> (all experiments were carried out with 0.5410.05 T CH<sub>2</sub>CClF). Experiments performed with other bath gases show a similar sharp increase in signal with pressure at low pressures, and a slow

decrease in signal with increasing pressure at higher pressures. The high pressure limit is imposed by the occurrence of dielectric breakdown. Figure 5 shows the dependence of the branching ratio (ratio of HF to HCl yields) on the intensity of the photolytic pulse. The high pulse energy limit stems from the limited output available at 10.632  $\mu\text{m}$ , while the low pulse energy limit is imposed by a decline in total signal with decreasing pulse energy.

A rate equations<sup>5,6</sup> model of the excitation-dissociation process can be used to interpret these results. While the rate-equations approach may not be a valid description of the excitation process under all conditions,<sup>7</sup> it probably describes optical pumping through the quasicontinuum adequately, and is particularly well suited to describe infrared laser induced chemistry at relatively high pressure, where collisions tend to disrupt coherent effects.<sup>8</sup> We thus anticipate that rate equations, with the proper choice of optical excitation and collisional deactivation models, will accurately reflect the pressure dependent behavior observed in these experiments. Further, to the extent that pumping through the quasicontinuum, rather than through the discrete lower levels,<sup>9</sup> determines the dissociation yield, the rate equations will also describe the power dependence of the competing dissociation channels.

Our rate equations are energy-grained into approximately 30 levels, with level separations corresponding to the energy of the incident laser photons,  $\sim 2.7$  kcal. The population of any energy level can be described by:

$$\frac{dN_i}{dt} = \sum_{j=0}^{30} k_{i \leftarrow j}^o N_j + k_{i \leftarrow j}^c N_j - k_{j \leftarrow i}^o N_i - k_{j \leftarrow i}^c N_i - \sum_k k_{ik}^d \quad (2)$$

Here, the superscripts "o" and "c" refer to optical and collisional processes, respectively, and  $k_{ik}^d$  refers to the rate of dissociation from level  $i$  via reaction channel  $k$ . Briefly, level zero is occupied by ground state molecules not accessible to the radiation field, while level one, which is degenerate in energy, contains molecules which are accessible to the photon field. Based on estimates of the power broadened laser linewidth, and width of the  $\nu_1$  vibrational feature, the  $t=0$  populations of these levels are given by  $N_1/N_0 \sim 0.02$ . Collisions are assumed to equilibrate levels one and zero at a gas kinetic rate. For all other levels,  $N_j=0$  at  $t=0$ . Optical pumping rate constants are products of absorption cross sections, degeneracy ratios and the laser intensity. For CH-CClF,  $\sigma_1 = 1.3 \cdot 10^{-19} \text{ cm}^2$ , and the level dependence is assumed to have the form  $\sigma_i = \sigma_1 i^{-1/2}$ . The laser pulse is assumed square,  $\tau = 25 \text{ nsec}$ ,<sup>10</sup> and  $I = 1.4 \cdot 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ . Level degeneracies are approximated by state densities based on the Whitten approximation,<sup>11</sup> with  $\omega = 976 \text{ cm}^{-1}$  and  $V = 1226 \text{ cm}^{-1}$ . Reaction rates are calculated from QRRK theory, with  $k = A \frac{(n+1) \cdot (n-m+1)}{(n-m+1)! (n+1)!}$ ; for HF elimination, the Arrhenius (A) factor is  $2.60 \cdot 10^{11} \text{ sec}^{-1}$ ,<sup>12</sup> and at threshold,  $m=21$ . A variety of models of collisional energy transfer were examined (vide infra) in order to best fit the experimental data.

The rate equations were numerically integrated, using a modified Gear algorithm,<sup>13</sup> on a Z-80A based microcomputer (North Star) containing 64K of RAM. Integrations typically required 2 hrs cpu time for each pressure. As noted above, a variety of energy transfer models<sup>14</sup> were used to simulate collisional deactivation of the optically pumped molecules, including step ladder, random and exponential models. A "best fit" was obtained using an exponential model with  $E = 2.5 \text{ kcal}$ . Results of this calculation are shown in Figure 4. The competitive dissociation processes can also be simulated via the rate equations, as shown in Figure 5. Here, the ratio of predicted dissociation rates is shown as a function of pressure, using  $A = 1.87 \cdot 10^{11} \text{ sec}^{-1}$  and  $m=22$  at threshold for the HCl elimination process. The rate equations thus apparently provide an adequate description of the excitation process, and may provide insight into the mechanistic details of multiphoton dissociation processes.

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#### Figure Captions

Figure 1. Schematic of experimental apparatus. The infrared detector is L-N<sub>2</sub> cooled InSb. Total response time of the system is  $\leq 0.5$   $\mu$ sec.

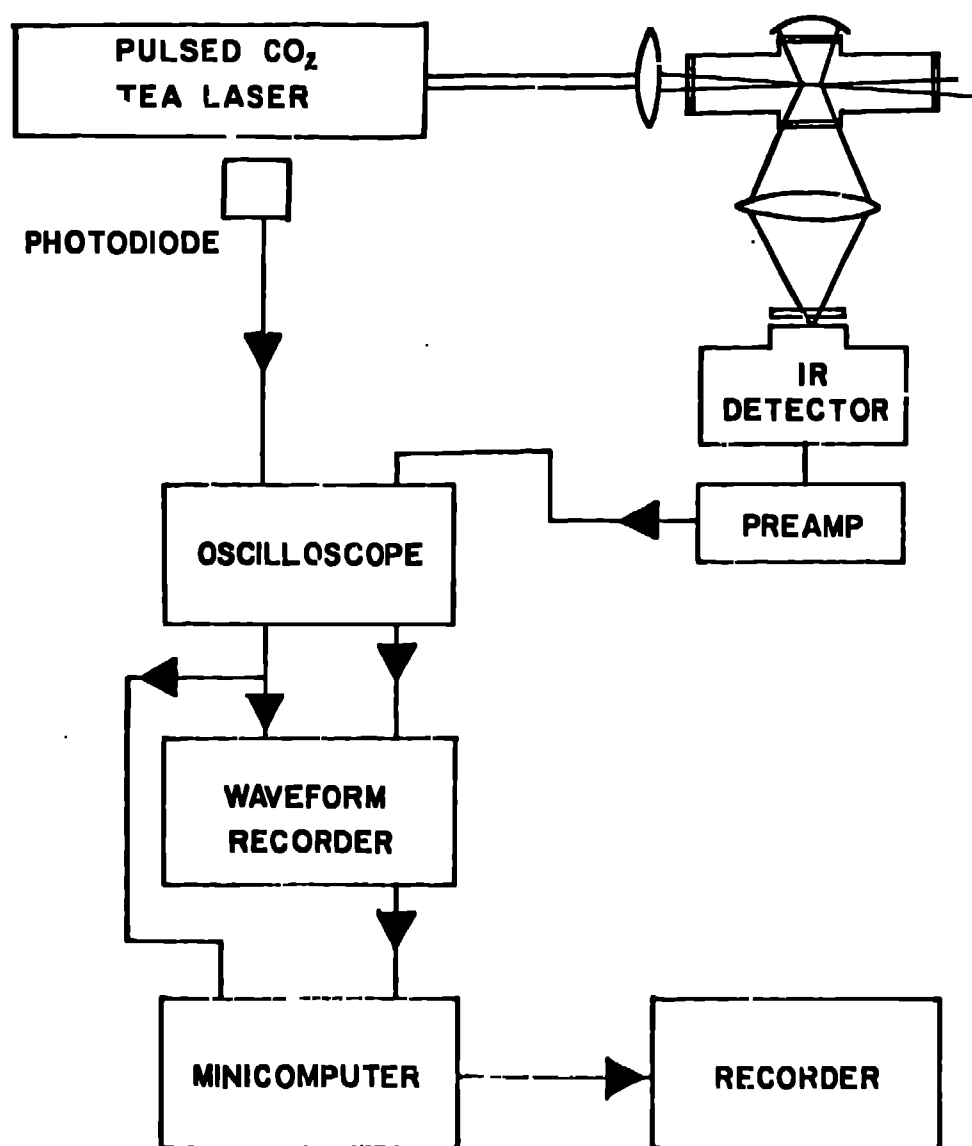
Figure 2. Emission in the region 2.0-2.7  $\mu$ m, due to HF fluorescence.

Figure 3. Emission in the region 3.1-4.1  $\mu$ m. The fast-decaying component is assumed due to fluorescence from the quasicontinuum of CH<sub>2</sub>=CFCl, while the slow decaying component is due to HCl fluorescence.

Figure 4. Dependence of the HF yield on N<sub>2</sub> pressure. Yields are taken from the t=0 intercept of the semilog plots of fluorescence decays. Experimental data, ●; numerical simulation, □.

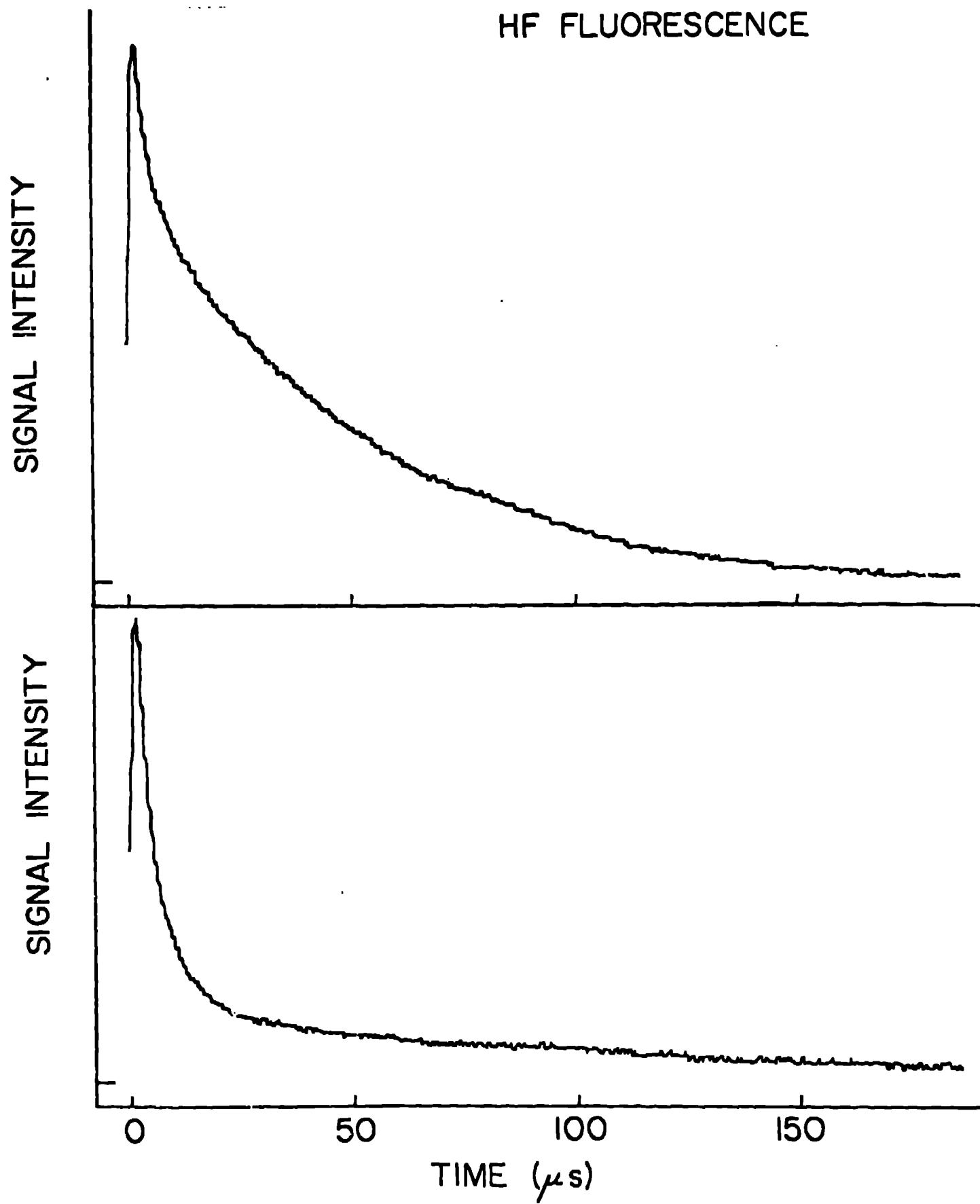
Figure 5. Dependence of the HCl/HF branching ratio on laser pulse energy. Experimental data, ●; numerical simulation, ▲.

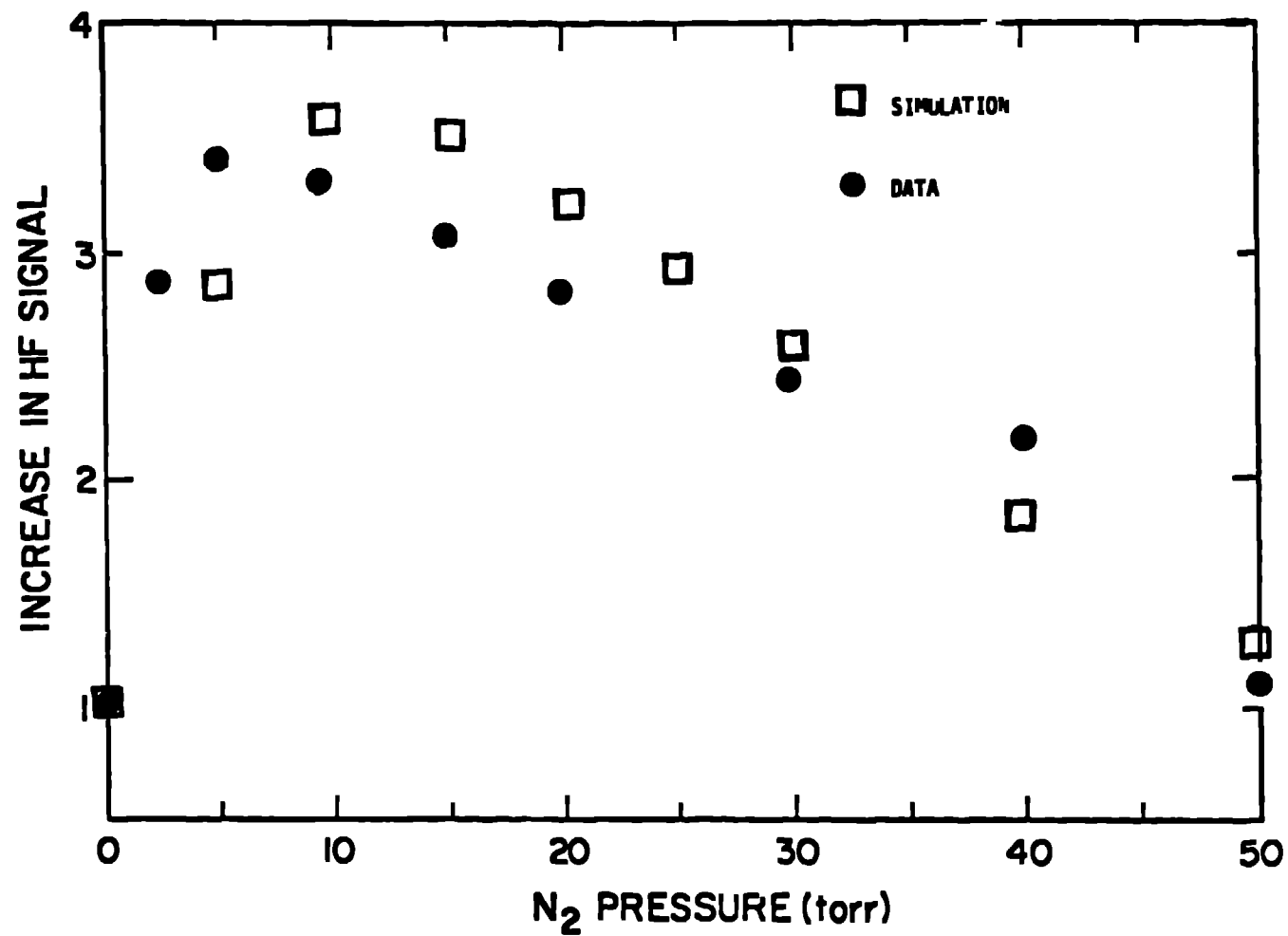
# EXPERIMENTAL



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